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Silicon-Doped Aluminum Clusters

$Si@Al_{56}[N(2,6\text{-}iPr_2C_6H_3)SiMe_3]_{12}$: The Largest Neutral Metalloid Aluminum Cluster, a Molecular Model for a Silicon-Poor Aluminum–Silicon Alloy?**

*Michael Huber, Andreas Schnepf, Christopher E. Anson, and Hansgeorg Schnöckel**

Dedicated to Professor Heinrich Nöth on the occasion of his 80th birthday

A few years ago, we presented $Al_{38}(AlCp^*)_{12}$[1] (**1**, $Cp^* = C_5Me_5$), which was the largest neutral structurally characterized metalloid cluster compound containing "naked" metal atoms.[2,3,6] Many other metalloid aluminum clusters[7] present a topology of aluminum atoms similar to the face-centered-cubic (fcc) lattice in solid aluminum metal. In contrast, **1** exhibits a $Al_8Al_{30}(AlCp^*)_{12}$ structural motif (see the Supporting Information). To investigate the poorly understood influence of the ligand system on the structure of metalloid aluminum clusters, we focused our attention on a modified amide ligand. In this ligand, one of the $SiMe_3$ groups of the previously employed $N(SiMe_3)_2$ entity was substituted by the bulkier dipp ligand (dipp = 2,6-$iPr_2C_6H_3$). In analogy to $Sn_{15}R'_6$ (**2**, $R' = N(dipp)SiMe_3$)[8] and to the silicon-centered metalloid aluminum cluster $Si@Al_{14}Cp^*_6$ (**3**, Figure 1),[9] we synthesized the cluster $Si@Al_{14}R'_6$.[10] Furthermore, we obtained a small number of crystals of an $Al_{48}R'_{12}$ cluster.[11,12] Subsequently, we varied the reaction conditions dramatically to optimize the synthesis of this cluster and to obtain other clusters containing silicon atoms.[13] Thus, we were able to synthesize $Si@Al_{56}R'_{12}$ (**5**), in which a $SiAl_{44}$ core is protected by twelve cuboctahedrally arranged $Al[N(dipp)SiMe_3]$ units. The structure and bonding situation in **5** is drastically influenced by the single foreign atom in the center.[16] We demonstrate herein that this cluster compound not only exhibits an initially unexpected structure, but that it is also the largest structurally characterized neutral metalloid cluster containing "naked" metal atoms known to date.

A metastable solution of AlCl, obtained by the simultaneous condensation of the high-temperature AlCl molecule and toluene/Et_2O (3:1),[17] is treated with a suspension of $Li[N(dipp)SiMe_3]$ in toluene at temperatures near 120 °C after a thermal treatment (see the Experimental Section). After workup, black, cubic crystals of **5** were obtained. Energy-dispersive X-ray spectroscopy (EDX) measurements of the crystals showed an Al/Si ratio of approximately 4.16:1 (calcd 4.30:1).

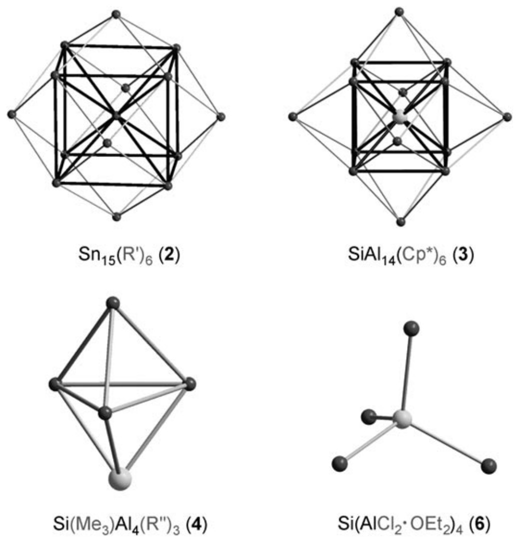

Figure 1. Central units of the compounds **2**, **3**, **4**, and **6** ($R'' = Si(SiMe_3)_3$).

The crystal structure analysis reveals the molecular structure of $Si@Al_{56}R'_{12}$ (**5**; Figure 2).[19,20] Table 1 compares the observed and calculated distances (numbering scheme as in Figure 2). The observed Si−Al and Al−Al distances in **5** are

Table 1: Selected bond lengths (in pm) for **5** at 100 K (experimental) and calculated for **5′** (see also Figure 2 c and text).

	Av (min/max)	calcd
Si1–Al4(Al5)	243.3 (243.3/243.3)	245.4
Al1–Al2	281.2 (280.5/282.7)	282.3
Al1–Al3(Al3′)	301.4 (299.3/308.8)	300.1
Al1–Al4	308.5 (306.8/309.9)	312.9
Al2–Al2	278.7 (272.8/285.7)	274.7/285.2
Al3–Al3′	279.7 (279.3/280.2)	281.4
Al4–Al4(Al5)	397.4 (397.2/397.5)	400.7
$Al2_{cub}$–$Al2_{cub}$[a]	254.2 (254.0/254.5)	256.8
Al_L–Al[b]	262.2(259.10/265.5)	266.9/263.2
Al_L–N	179.9(179.6/180.3)	–

[a] Aluminum atoms that connect two cuboctahedra. [b] Al_L are the ligand-bearing aluminum atoms.

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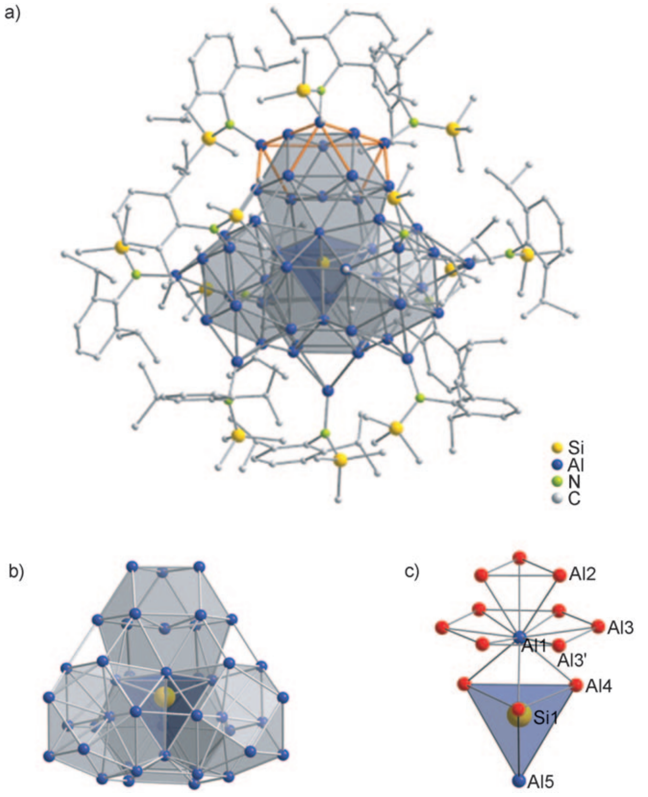

Figure 2. a) Molecular structure of $Si@Al_{56}[N(dipp)SiMe_3]_{12}$ **5**. The conjunction of three AlR′ groups of the outer $Al_{12}R'_{12}$ cuboctahedron (see Figure 3 a) is marked by orange sticks. The H atoms are omitted for clarity. b) The "naked" $SiAl_{44}$ core of **5** built from four Al_{12} cuboctahedra. c) The fcc coordination of the aluminum atoms in the $SiAl_{44}$ core for one of the four Al_{12} cuboctahedra in **5**. There are only five unique aluminum atoms (Al1–Al4 and Al3′), owing to the C_3 symmetry operation.[18]

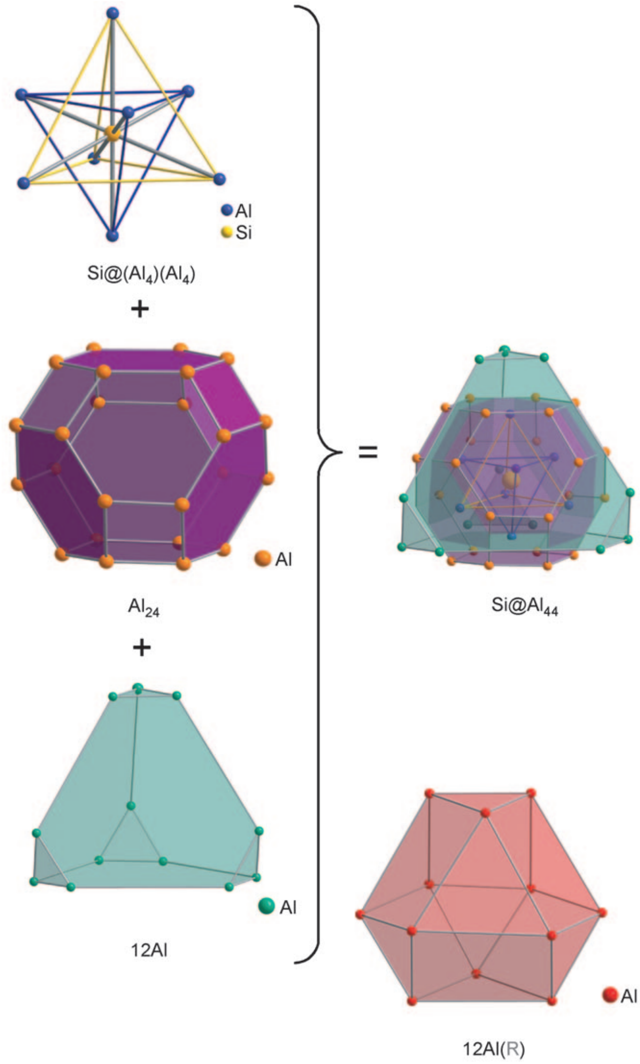

Figure 3. Alternative shell description of **5**. In the center of the cluster, a silicon atom is surrounded by two Al_4 tetrahedra. The next shell contains 24 aluminum atoms, which form a truncated octahedron (violet). It is surrounded by 12 aluminum atoms in a truncated tetrahedron (turquoise). These 45 "naked" metal atoms (1 Si + 44 Al) form the cluster core. The 12 ligand-bound aluminum atoms in the outer shell are arranged in a distorted cuboctahedron (red).

in accordance with the measured distances in other metalloid Si/Al clusters. Furthermore, the agreement with the calculated distances in the model compound $Si@Al_{56}(NH_2)_{12}$ (**5′**) confirms the congruence of theory and experiment found for many other metalloid clusters. The distances in Table 1 not only reflect those of the cuboctahedron shown in Figure 2 c, but they refer to all four Al_{12} cuboctahedra in the $SiAl_{44}$ core of **5**. A central silicon atom is tetrahedrally surrounded by four aluminum atoms at a distance of 243 pm. The four triangular planes of this Al_4 tetrahedron are the basal triangular planes of four Al_{12} cuboctahedra, resulting in a $SiAl_{44}$ framework of "naked" atoms for the cluster core. Twelve ligand-bearing aluminum atoms forming another cuboctahedron are located on the three rectangular planes of each of the four central Al_{12} cuboctahedra of the $SiAl_{44}$ core. An alternative shell description of the $SiAl_{56}$ framework (Figure 3) clarifies the connection between the four central Al_{12} cuboctahedra and the resulting distorted cuboctahedral arrangement of the outer twelve AlR′ units. In the crystal lattice of **5**, the $SiAl_{56}R'_{12}$ cluster molecules are in a cubic-primitive arrangement. In some experiments, a tetrahedral $Al_4(SiMe_3)_4$ cluster molecule was incorporated to give **5a**, which displays an almost CsCl-type structure.[21]

NMR spectra of **5** and **5a** could not be obtained, as crystals of **5** and **5a** are insoluble in common solvents.[25] Neither in the solid-state EPR spectrum nor in SQUID measurements was a signal observed, thus excluding the presence of a Al_{57} cluster radical with an aluminum atom rather than a silicon atom in the center. DFT calculations on the model compound **5′** demonstrated that the experimentally observed structure of **5** is also a local minimum of **5′**, with an energy 239 kJ mol^{-1} lower than for the hypothetical compound $Al@Al_{56}(NH_2)_{12}$.[27] The energy balances of **5′** and **1** as intermediates on the way to the elements are shown in Figure 5 (see below).

At first glance, the formation of **5** seems to be unexpected. However, the preparation of **3** (Figure 1) has shown that $[SiCp^*_2]$, for example, can serve as a silicon source for the formation of a silicon-centered aluminum cluster.[9] During the formation of the polyhedral $SiAl_4$ cluster **4** (Figure 1), incorporation of silicon atoms into the cluster system also proceeds by partial fragmentation of the $Si(SiMe_3)_3$ ligand.[14] For the $N(dipp)SiMe_3$ ligand, fragmentation has been observed earlier and was detected during the synthesis of **5**;[28] that is, the known species $Li[Al\{NH(dipp)\}_4]$ could also be isolated.[29] Apparently, the very slow decomposition of the ligand and the slow release of reactive silicon-containing species are absolute requirements for the formation of the silicon-poor cluster **5** and its growth around the structure-determining silicon center. Temperatures above 100 °C are essential for this complex formation process. A model for the primary formation of a tetrahedral $SiAl_4$ center during the formation of **5** should be a tetrahedral compound, in analogy to the formation of **3** from the halide $Si(AlCl_2{\cdot}Et_2O)_4$ (**6**, Figure 1), which was characterized by crystal structure analysis and is an intermediate on the way to **3**.[9,30]

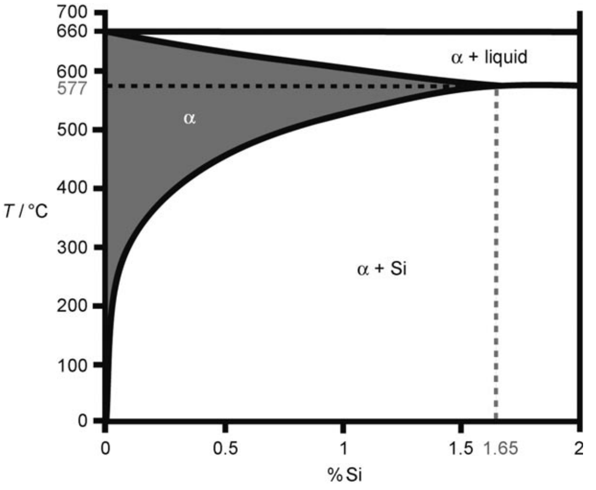

Figure 4. Section of the phase diagram for the two-component system Al–Si up to a silicon concentration of 2%. The maximum solubility of silicon in aluminum is 1.65% at 577 °C.

It is noteworthy that in **5**, the silicon atom is situated at a tetrahedral site, that is, there is no substitution of aluminum by silicon as is found, for example, in Si/Ga clusters in mass spectrometric experiments ($SiGa_{12}$, $SiGa_{22}$)[15] or in zeolites (SiOAl compounds). This result is in accordance with the Al/Si phase diagram (Figure 4), in which silicon-poor mixed crystals are only observed in an area of less than 2% Si.[31] As far as we know, no structural information of this mixed crystal phase has been reported to date.[32] The concentration of silicon in compound **5** is very similar to that in the mixed crystal phase, hence it should be possible to transfer the experimentally obtained structure of **5** to microcrystalline areas of the mixed crystal phase in the Al/Si phase diagram.[34]

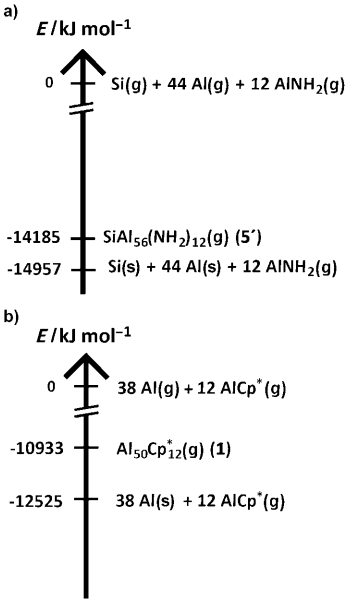

Figure 5. Calculated energy diagram for a model reaction from the gaseous metal atoms (Si, Al) and the AlR molecules (R = NH_2, Cp*) to the elements via the cluster compounds a) **5′** and b) **1**.

The special stabilization of the metalloid aluminum framework of **5** by incorporation of one silicon atom is clearly demonstrated in Figure 5. The molecular model compound **5′** is only destabilized by about 772 $kJ\,mol^{-1}$ in comparison to the solid elements aluminum and silicon and to molecular $Al(NH_2)$, whereas **1** is destabilized by about 1600 $kJ\,mol^{-1}$ relative to its components. This stabilization of a silicon-centered $SiAl_{44}$ framework in **5** compared to an Al_{38} framework in **1** is also demonstrated by the calculated atomic volumes based on experimental structural data. The average atomic volume of each of the 45 atoms in the $SiAl_{44}$ framework in **5** (28.71 Å^3) is about 2% smaller than that in **1** (29.25 Å^3).

Solid-state ^{29}Si and ^{27}Al NMR spectra are not yet available. Therefore, the following discussion of the bonding situation is based on the calculated chemical shifts. For the central silicon atoms in **5′** and **3**, values of $\delta = 0$ and -455 ppm, respectively, were obtained. The population analysis results in partial positive charges of $+0.8$ and $+0.3$. Hence, the significant difference in chemical shift is not based on charge effects but on different paramagnetic shielding effects.[35] The paramagnetic shielding term is inversely proportional to the electronic energy and therefore to the HOMO–LUMO gap. Thus, the following interpretation of the ^{29}Si chemical shifts results. Compound **3** is stabilized because of its jellium-like electronic structure (40 electrons);[36–39] the consequently large HOMO–LUMO gap of 1.7 eV is accompanied by an extreme upfield shift of the ^{29}Si signal. In contrast, the calculated HOMO–LUMO gap in **5′** is only 0.5 eV, and therefore the ^{29}Si signal is shifted downfield to 0 ppm. This interpretation is supported by the deep red color of **3** and the metallic black color of **5**, suggesting that **5** is on the way to the metallic state. Consequently, on the basis of the Knight shift, we should expect a less shielded ^{29}Si signal in the Si/Al α mixed crystal phase.[40,41] The special metalloid bonding situation in **5** does not contradict the jellium model, because a stable electronic state would be achieved with 156 electrons; in agreement with the smaller HOMO–LUMO gap,[42] the sum of the valence electrons in **5** is 160 ($44 \times 3 + 12 \times 2 + 4$). Therefore we favor, as has been applied to other metalloid clusters, a shell-like description for **5** (and for **3**) over other models.[43,44] Consequently, it is highly justified to describe **5** as a superatom modified or functionalized by a central silicon atom.[45]

If only the "naked", not ligand-bound, metal atoms are considered, **5** is larger than the recently described Pt@Pd_{164-x} cluster **7** (43 "naked" atoms in the Pt@Pd_{42} core)[6] and Au_{102} cluster **8** (39 "naked" gold atoms);[47] in fact, cluster compound **5** is actually the largest structurally characterized neutral nanoscale "metal ball". In **7** and **8**, the ligands not only form a protecting shell for the cluster core but also the glue between the inner and outer palladium and gold shells (see the Supporting Information).[48,49]

In summary, our results demonstrate that a very small amount of "impurity", especially in metalloid systems, can have drastic effects on the structure of nanoscale particles. These impurities are only detectable by single crystal structure analysis; using STM or AFM, it would be impossible to identify such details, and **5** might be misinterpreted as an Al_{55} cluster. Therefore, these results are sobering, both for the preparation and for the interpretation of nanoscale species. On the other hand, the realization that one central atom, which contributes only one more electron and proton to the large number of surrounding metal atoms, can determine the structure and therefore the properties of a nanoscale species, offers a chance for the synthesis of tailor-made clusters. Regarding the functionalization of such cluster compounds, we could also focus on the substitution of the silicon atom by transition-metal atoms with special magnetic behavior. As in crystalline **5**, it might be possible to insert magnetic centers into a metallic matrix instead of obtaining a structure of nanoseparated silicon atoms in a cubic-primitive arrangement. Such considerations are the subject of current experiments.

Experimental Section

All manipulations were carried out under nitrogen atmosphere with solvents predried by standard procedures. The preparation of the metastable AlCl solution[17] and Li[N(dipp)$SiMe_3$] were prepared as described in the literature.[50]

Compound **5** was synthesized by the reaction of a suspension of Li[N(dipp$SiMe_3$] (5 mmol, 1.28 g) in toluene (10 mL) and AlCl (4.5 mmol) in toluene/Et_2O (3:1, 14 mL). After a thermal treatment of the AlCl solution at 60 °C for 30 min, the two reactants were combined at room temperature, and the solution changed color to dark brown. After the reaction mixture was stirred for two hours at room temperature, it was warmed to 80 °C in a few steps. Precipitated LiCl was separated by cooling the reaction mixture to room temperature and subsequent repeated concentration. After removal of the solvent under vacuum and subsequent extraction with *n*-heptane, the reaction mixture was heated to 120 °C and held at this temperature for seven days. After this period, black cubic crystals of **5** could be obtained, which were suitable for X-ray analysis. The synthesis could be modified by directly warming the reaction mixture to 120 °C. Furthermore, crystals could be obtained from extracts of toluene, *n*-pentane, and [D_6]benzene. The overall yield was 12 mg; a percent value does not seem logical because of the formation of metallic aluminum during the synthesis. NMR spectroscopic measurements in solution could not be performed because of the insolubility of **5** in common solvents. Mass spectrometric investigations (IONSPEC ULTRA FT/ICR MS with a CRYOMAGENTICS 7 Tesla magnet) with the LDI method resulted in fragmentation of **5**.

Quantum chemical calculations were performed with the TURBOMOLE package.[51] The RI-DFT module (BP86 functional with the SV(P) basis set) was used for all elements. NMR shifts were obtained using the MPSHIFT module.

The molecular volumes were calculated using the Gaussian03 system at the SCF level with 3-21G* basis sets.[52] Single-point calculations based on experimental geometries of the cluster compounds were performed using the ICPM solvation model.

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[3] We have described those clusters as "metalloid" which contain both ligand-bearing and "naked" metal atoms exclusively bonded to other metal atoms to express, in accordance with the Greek word ειδος (ideal, prototype), that the ideal form of the solid-state structure can be recognized in the topology of the metal atoms in the clusters. In general, such metalloid clusters contain more direct metal–metal contacts than metal–ligand contacts.[4] The metal-rich clusters $[Al_{77}R_{20}]^{2-}$ and $[Al_{69}R_{18}]^{3-}$ ($R = N(SiMe_3)_2$) are anionic in the solid state.[5,6]

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[11] For this $Al_{48}R'_{12}$ cluster compound, the following lattice constants were obtained $[Li(OEt_2)_3]_2$-$[Al_{48}(NSiMe_3dipp)_{12}\cdot 3\,C_7H_8]$: triclinic, $P\bar{1}$, $a = 20.2286(15)$, $b = 20.5317(15)$, $c = 20.7166(16)$ Å, $\alpha = 80.823(6)$, $\beta = 68.234(6)$, $\gamma = 78.389(6)°$, $V = 7793.1(10)$ Å^3.[12]

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[13] The formation of silicon-centered or silicon-substituted aluminum clusters at drastic conditions is not unexpected, because we obtained such structural variations during the synthesis of a $SiAl_4$ cluster[14] **4** and during the detection of Ga_nSi_m clusters in mass spectrometric investigations.[15]

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[16] This modification relates, for example, to the $Al_{48}R'_{12}$ cluster[11,12] but also to other Al_nR_m clusters such as **1**.

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[18] Two of three remaining cuboctahedra are generated by performing a C_3 operation on one of the three cuboctahedra.

[19] Crystal data of **5** ($Si_{13}Al_{56}C_{180}N_{12}H_{312}$): $Z=8$, $f_w=4520.46\,g\,mol^{-1}$, crystal size: $0.26\times0.14\times0.12\,mm^3$, cubic, space group $Pa\bar{3}$, $a=39.1908(8)$ Å, $V=60194$ Å^3 (2), $\rho_{calcd}=0.998\,g\,cm^{-3}$, $F(000)=23688$, $\lambda=0.71073$, $T=100(2)$ K, $\mu(Mo_{K\alpha})=0.257\,mm^{-1}$, Bruker SMART Apex CCD area detector, 77844 reflections, 7903 unique ($R_{int}=0.1159$), structure solution using direct methods, refinement on F^2 ($2\theta_{max}=37.74°$), 5282 unique (2σ), H atoms were calculated, 784 parameters, 0 restraints, $R_1(I>2\sigma(I))=0.0617$, wR_2all data) $=0.1622$, GooF(F^2) $=1.044$, restricted GooF $=1.044$, ρ(e)(min/max) $=-0.380/0.628$ e Å^{-3}; computer programs ShelXTL 6.14, SMART NT 5.6, SAINT+ 6.45, SADABS; unit cell determination: 19151 reflections, multiscan absorption correction, $T_{min}/T_{max}=0.9330/0.9683$. Because of the large remaining volume inside the unit cell which is accessible for solvent molecules, with the application of a rotating anode as an irradiation source and a five-minute irradiation time (CCD detector), no reflections with an intensity of $2\theta>37.74°$ could be observed. Assuming a large number of distorted toluene molecules in the unit cell, we have corrected the data with the Squeeze module integrated in the PLATON software. This procedure leads to the presence of assumed twelve toluene molecules per cluster.

[20] Crystal data of **5a** ($Si_{17}Al_{60}C_{192}N_{12}H_{348}$): $Z=8$, $f_w=4921.16\,g\,mol^{-1}$, crystal size: $0.26\times0.12\times0.08\,mm^3$, cubic, space group $F\bar{4}3c$, $a=40.929(5)$ Å, $V=68564$ Å^3 (15), $\rho_{calcd}=0.954\,g\,cm^{-3}$, $F(000)=20816$, $\lambda=0.71073$, $T=150(2)$ K, $\mu(Mo_{K\alpha})=0.253\,mm^{-1}$, STOE IPDS2 area detector, 8475 reflections, 1404 unique ($R_{int}=0.1046$), structure solution using direct methods, refinement on F^2 ($2\theta_{max}=40.00°$), 544 unique (2σ), H atoms were calculated, 131 parameters, 0 restraints, $R_1(I>2\sigma(I))=0.1459$, wR_2(alle Daten) $=0.2381$, GooF(F^2) $=0.826$, restricted GooF $=0.826$, ρ(e)(min/max) $=-0.307/0.492$ e Å^{-3}; computer programs ShelXS 97, ShelXL 97, STOE IPDS software. Unit cell determination: 6125 reflections, Lorentz, polarization, and numerical absorptions correction; $T_{min}/T_{max}=0.9622/0.9698$. CCDC-683229 (**5**) und 683230 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] In **5a** there are two $Si@Al_{56}R'_{12}$ clusters A und A′ distinguishable only by a slightly modified topology of the twelve outer Al_{12} units. Because only every-other $Si@Al_{56}R'_{12}$ cluster can be copied onto itself by the symmetry operation, a structure results in which the fcc lattices of A and A′ are combined to a single lattice with the translation vector (0.5, 0.5, 0.5); that is, a formal NaCl structure is obtained that is built up of the cluster centers for A and A′. If each of the eight cubic sites (formerly the tetrahedral sites of the primary structures of A and A′) are filled with $Al_4(SiMe_3)_4$ units, a structure for **5a** similar to the CsCl type results. In analogy to the integration of these molecules, it may be possible to incorporate other species, for example, small C_{60} molecules, into the sites between the large "super metal atoms" of **5**. In this case, an inverse and modified situation in comparison to the superconducting fullerides (e.g. K_3C_{60})[22,23] would be obtained, in which the small metal ions (e.g. K^+) are located in the sites of the fcc lattice, which is built up of the large structure-determining $C_{60}{}^{3-}$ anions. Ongoing experiments to incorporate C_{60} into **5** have not yet resulted in crystalline substances.[24]

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